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14. ABSTRACT

Metal-containing clusters produced in molecular beams were used to explore the fundamental interactions in nanocatalysis and nanocluster materials. To probe nanocatalysis, we studied metal-adsorbate complexes with mass-selected infrared photodissociation spectroscopy. These studies investigated the carbonyl complexes of Ag, Au, Pt, Co, V, Nb, Ta, as well as those for small oxides of vanadium. IR photodissociation spectroscopy determined of the number of ligands in the primary coordination sphere, the shift in ligand/solvent vibrations compared to the free molecule, the structural arrangement of the ligands, and the electronic spin state of the metal. To probe nanocluster structure, bonding and stability, metal oxide, carbide and silicide clusters with up to 50 atoms were investigated with mass-selected photodissociation and density functional theory. Studies were completed on the oxide clusters of vanadium, niobium, tantalum, chromium, iron, yttrium, and lanthanum, copper and gold carbides and silicon clusters with chromium and silver. Clusters were identified with special stability (e.g., Cr4O10) and oxidation states were found to be different (e.g., iron) from those for the common bulk oxides. Copper and gold-doped carbon clusters adopt both linear and cyclic structures.

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Final Report

FUNDAMENTAL STUDIES AND ISOLATION STRATEGIES FOR METAL COMPOUND

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Abstract

Fundamental Studies and Isolation Strategies for Metal Compound Nanoclusters

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Objective: The goal of our research is an understanding of metal-metal and metal-ligand bonding relevant for the discovery of new nanocluster materials and the design of nanocluster catalysts. Metal bonding is fundamental in Chemistry, but these interactions are problematic for current theoretical methods. Laboratory measurements are therefore essential to guide the improvement of theory and to discover new materials. Because theory has limited predictive power, unanticipated structures may yet be discovered for metal-containing nanoparticles or their aggregates. Fundamental studies reveal the principles governing cluster growth, stability, and reactivity, thus enabling the rational design of nanocluster materials. We work to discover these principles and to apply them for real nanoparticle synthesis on a macroscopic scale.

Approach: Our approach is to study the properties of metal clusters in molecular beams, where experiments are possible with size selection and an exact knowledge of composition. Clusters are produced with pulsed laser vaporization, detected with time-of-flight mass spectrometry and studied with new forms of infrared laser spectroscopy. These studies focus on transition metal compounds (carbides, oxides, silicides) that are expected to have high stability, an essential property for their isolation. Photodissociation and IR spectroscopy experiments reveal stability and bonding patterns. However, clusters containing transition metals are often highly reactive. This forms the basis for catalytic activity, but it also introduces difficulties in their isolation as small particles. To understand catalytic activity and to design inert coatings for nanoclusters, we investigate their surface chemistry via adsorption of small molecules. In a parallel and co-dependent line of work, we employ a new flowtube reactor for macroscopic synthesis of ligand-coated nanoclusters. This device employs a high throughput laser vaporization source, a flow reactor for the application of ligand coatings and a low-temperature isolation trap for collection of ligand-coated nanoclusters in solution.

Statement of Objectives

Fundamental Studies and Isolation Strategies for Metal Compound Nanoclusters

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Metal-containing cluster molecules and nanoparticles are produced in the gas phase via laser vaporization of solid targets, and these species are studied with mass spectrometry and infrared laser spectroscopy. Metal carbide, oxide and silicide nanoclusters are studied in the size range from a few up to about 300 atoms. New infrared laser spectroscopy techniques investigate the vibrational spectroscopy of the nanoclusters themselves as well as those of molecular "adsorbates" attached to their surfaces. These nanoclusters are also evaluated for macroscopic synthesis via ligand coating in a new laser vaporization flowtube reactor apparatus. These overall experiments provide fundamental data for the structures, bonding stability and chemistry of metal atom clusters and they have the potential to discover new stable clusters that can be isolated and employed for "building block" materials.

Technical Proposal

Fundamental Studies and Isolation Strategies for Metal Compound Nanoclusters

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Introduction

Metal-containing clusters and nanoparticles provide new materials with unusual electronic, optical, magnetic and chemical properties.[1-7] The term "cluster" generally refers to particles smaller than a few hundred atoms, and "nanoparticle" generally indicates larger species with hundreds to thousands of atoms. Although their sizes are different, clusters and nanoparticles have many features in common. Both require special techniques for their preparation and study, and both may have properties that are different from those of the corresponding bulk materials. Although these systems have been the focus of intense investigation over the last 20 years, it is still not possible in most cases to predict the properties of clusters or nanoparticles. Quantum theoretical methods are gaining capability, but experimental work remains essential to the discovery of new systems and the elucidation of their behavior. In our research program, we focus on metal compound (carbides, oxides, silicides) clusters and nanoparticles. We produce these species in molecular beams with pulsed laser vaporization of solid targets. We investigate the structures of clusters and adsorbate molecules bound to their surfaces with mass spectrometry and new forms of infrared laser spectroscopy. In a parallel effort, we employ new strategies to isolate macroscopic amounts of clusters of these same materials, stabilized with ligand coatings.

Results of Work in the Prior Funding Period

Infrared Probes of Metal Cluster Structure and Bonding

Contract No. F49620-03-1-0044, January 1, 2003 to December 31, 2005

In the current funding period, we have made progress in several areas of metal cluster research, as summarized below. The papers published acknowledging AFOSR support are listed as references R1-R10. More details about this work and instrumentation photographs are available on our group web site at www.arches.uga.edu/~maduncan.

Metal Carbide Clusters

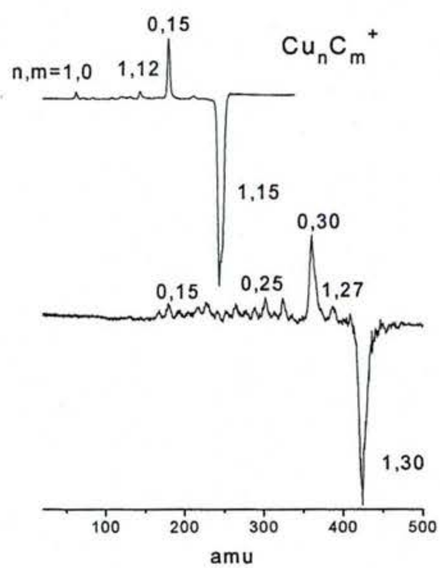
Transition metal carbides exhibiting the remarkable magic number at M_8C_{12} (M=Ti, V, Nb, etc.) were first reported by Castleman and coworkers.[8] These so-called "met-cars" clusters were speculated to have a cage structure with dodecahedral symmetry. Soon after this initial finding, our group reported other species with similar stability in the form of $M_{14}C_{13}$ (M=Ti, V, Nb) clusters.[9] These latter clusters are believed to have *fcc* structures and were denoted as "nanocrystals." Since this early work, met-cars and nanocrystal carbide clusters have been studied extensively[8-21] and they have been the subject of many theoretical calculations.[22-36] However, until recently, there was no spectroscopy on these species with vibrational resolution and there was no direct determination of their structures. In 1999, the former situation changed in an exciting way through our collaboration with Meijer and coworkers.[37-44] In this work, we developed an experiment using *infrared resonance enhanced multiphoton ionization* (IR-REMPI) to obtain vibrational spectra for these carbide clusters. This method relied on the "FELIX" free electron laser that provides high intensity tunable IR radiation in the

400-1800 cm^{-1} region, where carbide stretching modes are found. We first applied IR-REMPI to Ti_8C_{12} and $Ti_{14}C_{13}$,[37-38] and more recently these methods have been extended to other metal carbide[39-41] and oxide clusters.[41-44] With these vibrational spectra, we and others that have joined this effort[45-47] are able to test the structures predicted by theory for these clusters.

In recent work, we have extended the study of carbides to the noble metals and to silicon carbide.[R6] In the early transition metals, plasma reactions between metal vapor and added methane led to the formation of carbides, but this chemistry does not work for less reactive systems.[9] To form noble metal carbides, we use composite samples consisting of a carbon rod with an evaporated metal film coating. Laser vaporization of this composite sample produces the desired mixed clusters. To investigate the stability and structures of these systems, we use mass spectrometry and mass-selected photodissociation. In the past, copper-carbon clusters have been detected[48,49] and suggested to have metal-centered cage structures.[48] However, as shown in the example in Figure 1, photodissociation of MC_n^+ (M=Cu, Ag, Au) all find that the elimination of the neutral metal atom is the main fragmentation channel. This suggests that these clusters represent carbon species with metal attached externally.

Metal-Silicon Clusters

Transition metal-silicon clusters were first studied by Beck,[50] and there has been a recent flurry of both experimental[51-53] and theoretical[54-63] papers on these fascinating species. As in the metal carbide species, magic numbers are detected in the cluster distributions that grow under a wide variety of conditions. Magic numbers for iron, chromium, etc. transition metal species occur at MSi_{15}^+ and MSi_{16}^+, while copper has been found to have magic numbers at $CuSi_7^+$ and $CuSi_{10}^+$.[49] In both systems, the mass spectra have been interpreted to suggest that these species represent metal-centered structures, although there have been no direct structural measurements. We again employed laser photodissociation to probe the MSi_7^+ and MSi_{10}^+ clusters of the noble metals. We find that mass spectra for copper, silver and gold all have magic numbers at these two cluster sizes. However (Figure 2), photodissociation again occurs primarily by the elimination of metal, suggesting that these clusters are also not metal centered.



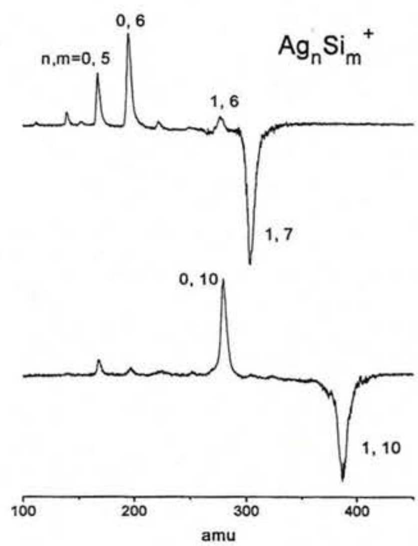


Figure 1. The photodissociation of CuC_{15}^+ and CuC_{30}^+ at 355 nm. The negative peak indicates parent ion depletion and the positive peaks are the fragment ions. Metal atom loss is the main channel for both.
Figure 2. Photodissociation of silver-silicon clusters at 355 nm. Metal atom loss is the main channel.

Metal Oxide Clusters

Metal oxide clusters are interesting for applications in surface science and catalysis,[64-68] as well as in solar energy conversion.[67-68] Mass spectrometry has been applied to these systems,[69-78] and they produce non-statistical combining ratios. Unlike metal carbide and silicides, there are no single magic numbered clusters, but rather at each metal increment there are several specific oxide stoichiometries. Structures have been predicted by theory involving M-O-M-O bonding networks.[79-85] Small oxides have been studied with matrix isolation[86] and photoelectron spectroscopy.[87-89] Our group, in collaboration with Meijer and coworkers, has employed IR-REMPI to obtain the first IR spectroscopy for these species in the gas phase in studies of Zr, Ti, Mg and Al oxides.[41-44] Because IR-REMPI failed for many other oxides, Fielicke and Meijer continued this work employing photodissociation spectroscopy with the free electron laser in a mass depletion mode of operation.[45-46] Asmis has employed depletion spectroscopy of mass-selected helium-tagged cluster ions (small $V_nO_m^+$).[47] In some systems, vibrational spectra have enough detail to suggest structures. However, especially for the transition metals, it is not yet clear which of the stoichiometries seen represents the most stable clusters. Neutral versus cation stability, as interpreted from mass spectral abundances, is often confused by different ionization/detection methods. We have employed photodissociation to investigate this.

Figure 3 shows the mass spectrum we obtain for $Ta_nO_m^+$ clusters, while Figure 4 shows photodissociation of selected Ta, V and Nb oxides. The signal/noise here is low because the clusters are difficult to fragment. We find two general channels for fragmentation. Clusters with excess oxygen lose either O_2 or O atoms to produce a smaller oxide with the same number of metal atoms. The data for $Ta_4O_{11}^+$ and $Ta_4O_{12}^+$ below illustrate this behavior. Clusters without excess oxygen tend to undergo fission, splitting off both metal and oxygen, producing a smaller oxide fragment. The stable oxides can then be identified as those clusters which do not lose oxygen only *and* which are produced repeatedly by fission of larger clusters. From studies like this of many $M_nO_m^+$ clusters of the metals V, Nb, Ta, we identify the n,m species 2,4; 3,7; 4,9; 5,12; and 7,17 as the most stable cation stoichiometries of these clusters.

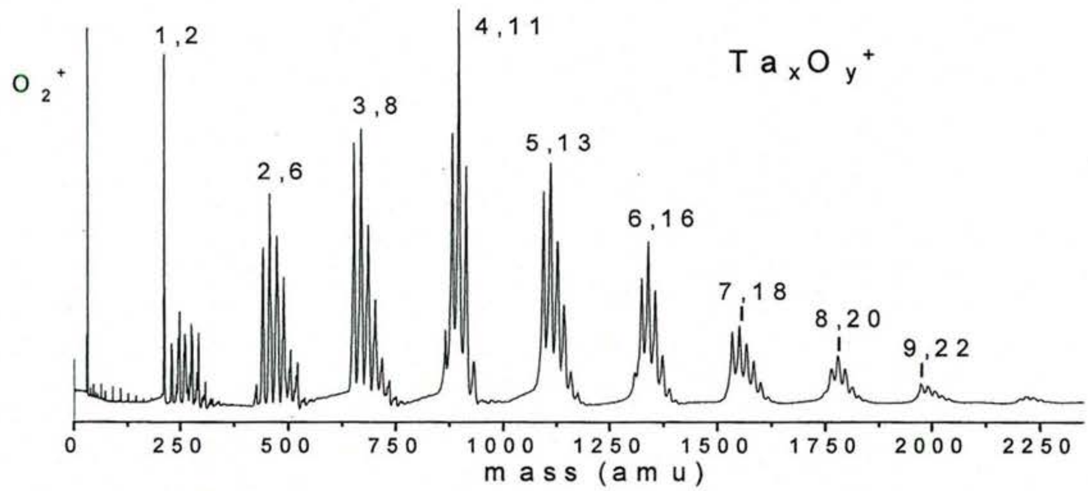


Figure 3. The mass spectrum of tantalum oxide clusters produced directly as ions from the laser plasma.

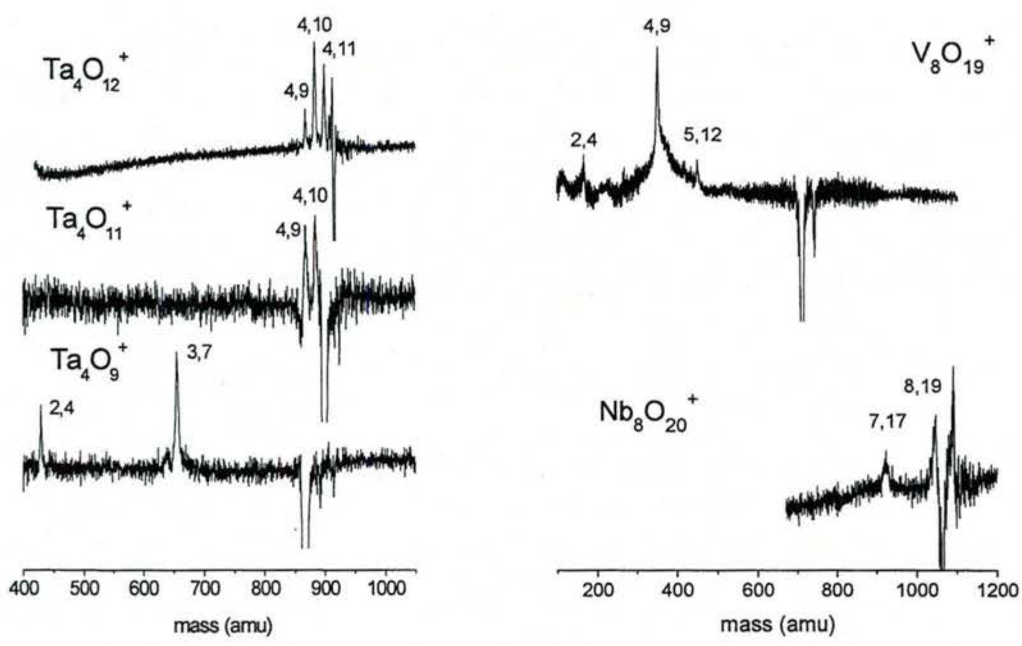
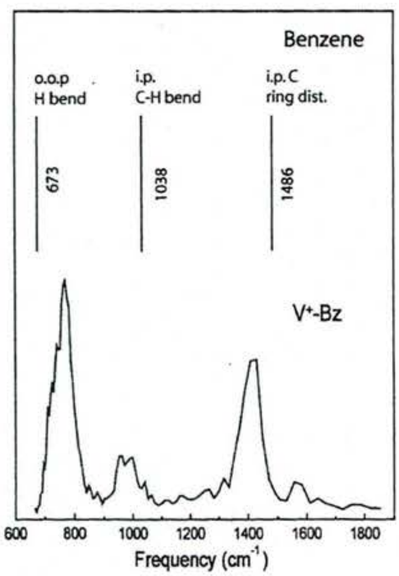


Figure 4. Photodissociation of Ta, V and Nb oxide clusters at 355 nm.

IR Spectroscopy of Metal-Molecular Complexes

A primary focus of our research program recently has been the development of IR spectroscopy for metal atom clusters and for metal-ligand complexes.[90-111] IR spectroscopy probes the details of the metal-ligand interaction in the same way that vibrational spectroscopy is applied to study adsorbates on metal surfaces.[64,65] We have shown that IR photodissociation spectroscopy can determine the ligand vibrational shifts that occur on binding to metal,[90-111] the coordination numbers of ligands around a metal ion,[97,99,103,104] and the presence of intracluster reactions as metals insert into ligand bonds[99,104] or as ligands couple with each other.[93,111] By comparison of spectra to those predicted by theory, structures and metal electronic states can be determined. We have employed the free-electron laser for studies in the mid-IR (400-1800 cm^{-1}), as shown in the spectrum of V^+(benzene) in Figure 5.[91] In the higher frequency range (2000-4500 cm^{-1}), we employ IR optical parametric oscillator (OPO) laser systems, as shown in the spectrum of $Mg^+(CO_2)_{1,2,3}$ in Figure 6.[94]



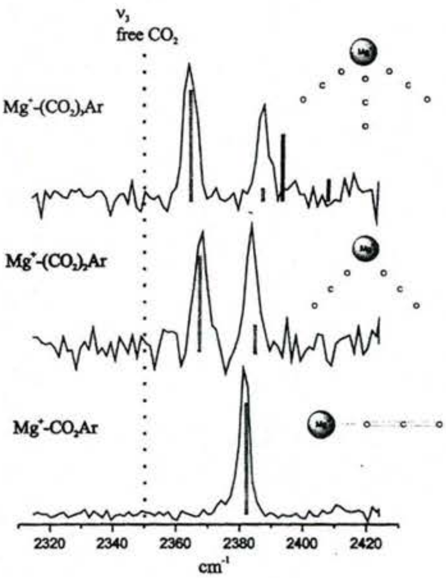


Figure 5. The IR photodissociation spectrum of V^+(benzene) measured in the fingerprint region with the free electron laser.
Figure 6. The IR photodissociation spectrum of $Mg^+(CO_2)_{1,2,3}$ measured near the asymmetric stretch vibration using an IR-OPO laser system and the rare gas tagging method. The structures shown correspond to the blue bands predicted by theory (Brinkmann and Schaefer at UGA).

Although metal-ligand binding energies often exceed the photon energy used to excite vibrational fundamentals, we have found that multiphoton excitation (with the free electron laser) or single photon excitation (with the OPO and the method of rare gas tagging[90,94-96,98-100,102-103,105-107,109]) can be used to obtain spectra with good efficiency for almost any desired metal-ligand complex. In our work for AFOSR (and related projects for DOE and NSF), we have obtained IR spectra for both main group and transition metal systems, as well as for atomic metal cation-molecular complexes and larger multi-metal atom clusters with adsorbates. AFOSR has supported the development of this area via DURIP funding for an Nd:YAG laser used to pump one of our OPO systems.

Synthesis of Cluster Materials

Although model studies in the gas phase are valuable, macroscopic amounts of clusters are needed to investigate their potential for new materials. We are therefore also working on the bulk synthesis of some of the same clusters that we have studied in the gas phase. Fullerenes or carbon nanotubes are typically produced via arc discharge sources.[112-115] Inorganic synthesis in solution is effective for semiconductor[4,7,116-118] or metal[4-7,119-121] quantum dots. However, while some metal oxide nanoparticles have been produced,[122-127] it is difficult to generate clusters containing transition metals. Laser vaporization is perhaps the most efficient way to make clusters from transition metals, but these species are produced in the gas phase. Real world applications require survival in air and solubility for convenient manipulation. Solubility is been obtained for quantum dots or noble metal colloids via ligand coating. To provide solubility and to stabilize our clusters, we desire a method that combines a cluster source with a ligand coating strategy. Andres has described a method in which a resistively heated oven or discharge source is combined in a high pressure gas flow with an injection of a ligand/solvent mixture using a nebulizer.[128] We have adopted a similar strategy, but retain the laser source for studies of transition metal clusters.

For these synthesis experiments, we have constructed a laser ablation flow reactor (*LAFR*; Figure 7).[127] It has a laser source scaled up to high repetition rates with a 100 Hz excimer laser, a flow tube for cluster growth, a ligand spray section to passivate cluster surfaces and a cooled trapping section where ligated clusters are collected in solution. The LAFR is operational and we have produced and isolated several new ligand-coated metal clusters, including $(TiO_2)_n(THF)_m$ and $V_nO_m(THF)_x$ in the size range of 20-50 total atoms.[127] In the present configuration, synthesis proceeds without any feedback on the operating conditions. However, we recently received DURIP funding for a differentially-pumped mass spectrometer system to monitor cluster growth. This system will include a reflectron time-of-flight mass spectrometer and an ArF excimer laser for photoionization detection. The vacuum system is under construction, and the full apparatus (shown in Figure 7) will come online soon.

We analyze the material that we isolate using our laser desorption time-of-flight mass spectrometer,[129] which is located in the synthesis lab a few feet away from the LAFR, or with other conventional materials analysis instrumentation (IR, UV-VIS, SEM, TEM). The mass spectrometer has been employed for many previous studies of cluster materials,[129] and it has been used in a collaboration with an undergraduate research program at Valdosta State University.[R8,R9] Figure 8 shows the mass spectrum of ligand-coated vanadium oxide clusters that were produced by vaporization of a titanium rod with a ligand spray of THF. The oxides are believed to be formed via metal reaction with the THF itself. The oxide stoichiometries isolated here are mainly the same ones identified as stable in our molecular beam experiments.

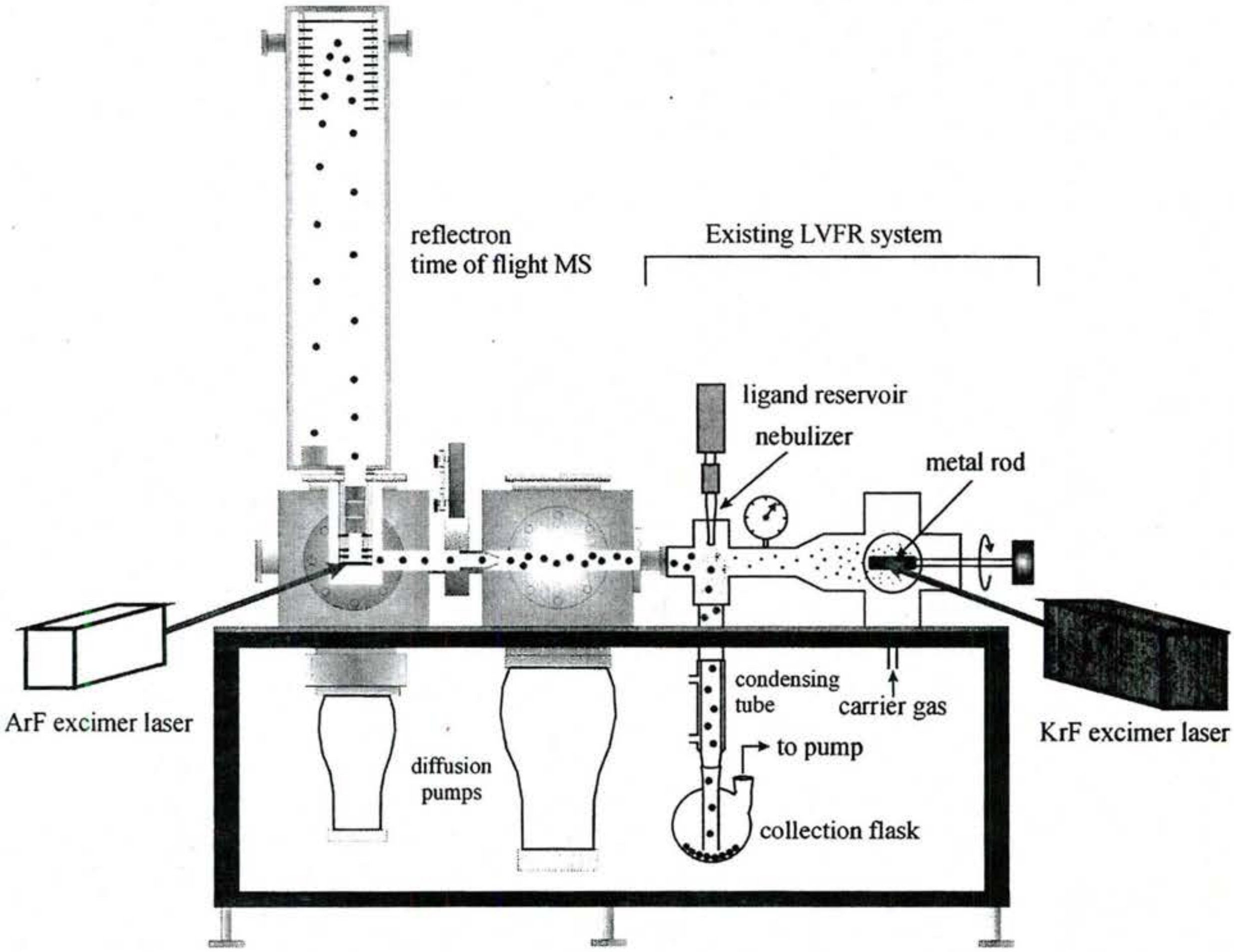


Figure 7. The laser vaporization flow tube reactor, with high intensity KrF laser for cluster production, differential pumping, reflectron time-of-flight mass spectrometer and ArF laser for photoionization.

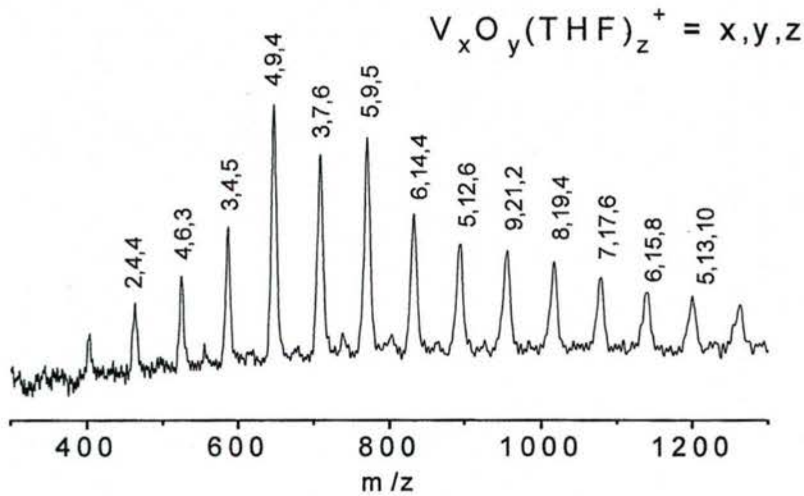


Figure 8. The mass spectrum of reaction products generated in our LAFR instrument by vaporizing vanadium and combining the metal vapor with a ligand stream of THF. The resulting solution was transferred to a remote mass spec for analysis.

New Research Directions

Introduction

Metal compound clusters have high bond energies and are generally less reactive than pure metal clusters. Stability and lower reactivity are favorable characteristics for nanoparticle isolation. However, the properties of oxides, carbides and silicides provide a rich variety of chemistry relevant not only for nanoparticles but also for surface science and catalysis. We therefore plan to continue to focus our research program in this area. We will use mass spectrometry and fixed-frequency photodissociation to investigate cluster dissociation channels and relative stability. We will continue to develop tunable laser IR spectroscopy to probe the vibrations of metal clusters and their molecular ligands or adsorbates. Finally, we will expand our effort in the controlled synthesis of nanoparticle materials with our flow reactor system.

Laser Photodissociation at Fixed Wavelengths

Mass spectra of pure transition metal clusters rarely deviate from a smooth distribution, but metal oxide, carbide and silicide mass distributions often contain magic numbered clusters or non-statistical combining ratios. These features are intriguing, but it is difficult to establish firmly the root cause of these distributions. Cluster growth kinetics and dynamics, neutral stabilities, ionization mechanisms, cation stability and fragmentation channels all play a role in the appearance of mass spectra. We have found that the distributions of clusters detected in this way are often misleading. Mass-selected photodissociation experiments provide a clearer indication of which clusters are more stable, as stable cations or neutral leaving groups tend to be produced repeatedly from the fragmentation of larger clusters. We have performed extensive studies of the mass-selected dissociation of transition metal carbide clusters,[9] and are finishing up studies of the noble metal carbides. Except for preliminary work by Beck,[50] our studies on noble metal species are the only ones to our knowledge on the photodissociation of metal-silicon clusters. Likewise, Castleman and coworkers have investigated some dissociation of vanadium oxide clusters,[72b] but our recent study on V, Nb, and Ta is the only other work on transition metal oxides. On the other hand, interesting and often unexplained magic numbers have been seen in the mass spectra of almost all metal-silicon and metal-oxide clusters studied. We will therefore focus this work on the non-noble transition metal-silicon clusters (V,Fe,Cr,Co,Ni, etc.) and on a variety of other transition metal (Fe, Cr, Co, etc.) oxide species. The goal is to identify stable clusters that may be isolated in the future and also to refine the capability of theory to predict which clusters are more stable.

As usual in mass spectrometry, we are keenly aware of mass coincidences and isotopic distribution issues. For example, iron (56 amu) and silicon (28 amu) have a readily identified coincidence, as do Ti (48 amu) and three oxygens or Zn (64 amu) and four oxygens. Multiple metal atoms with multiple isotopes yield distributions that broaden mass peaks at our finite resolution, and so single isotope metals are preferred for these studies (e.g., V, Co, Nb, Y, Ta). These issues will guide our choice of systems to study. In cases where there is special interest, it is of course possible to use isotopically substituted species to aid in mass spectral interpretation.

IR-REMPI studies and theory have identified the likely structures of small vanadium-oxide clusters,[47,72,75,76,80,85] and our work has clarified the relative stability of oxygen-precise frameworks versus clusters with excess oxygen. For example, our studies of $V_nO_m^+$ clusters indicates that the $V_2O_4^+$ species (calculated structure shown below), is produced as a photofragment from larger clusters, while $V_2O_2^+$ is not. Likewise, a symmetric structure can be drawn for $V_3O_7^+$, and this cluster is produced as a fragment from many larger ones, confirming its stability. However, the mass spectrum of clusters produced initially has more intense peaks at other stoichiometries.[72,75,76] We find the same trends for V, Nb and Ta oxide clusters, i.e., the n,m species 2,4; 3,7; 4,9; 5,12; and 7,17 are the most stable cations, but these are not the most abundant clusters that grow. Remarkably, these same stable stoichiometries are produced in our isolation experiments on ligand coated V_nO_m clusters. We hope to obtain similar information for other metal oxide species (Co,Y,Fe,Ni, etc.) to stimulate theory to explain and eventually predict such structures.

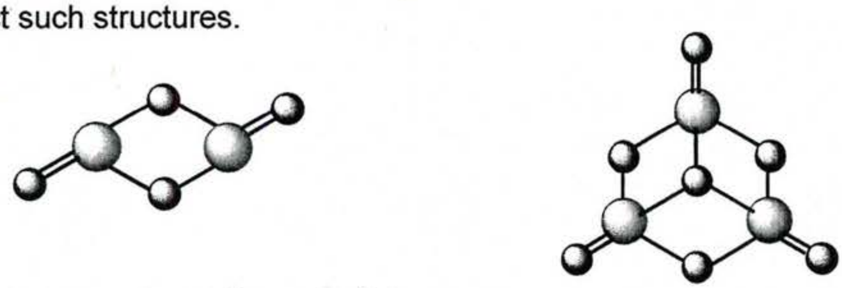


Figure 9.. Structures calculated for $V_2O_4^+$ and $V_3O_7^+$ clusters.

We have shown that noble metal-silicon clusters do not likely have metal-centered structures. However, the mass distributions for Fe, Cr, W and other mid-series transition metal-silicon species have different magic numbers at MSi_{15}^+ and MSi_{16}^+.[50,51] Theory has predicted metal centered structures for these species,[54-63] and preliminary photodissociation work by Beck is consistent with this.[50c] We will investigate these systems thoroughly with photodissociation to identify the stable clusters and whether or not they are likely to have metal-centered structures.

Because of our interest in noble metal clusters supported on oxide surfaces (see below), we will also attempt to make cluster analogues of these systems, e.g., $Au_x(V_nO_m)^+$. Photodissociation of these species can address whether the noble metal is integrated into the metal oxide network or segregated on its surface.

Infrared Spectroscopy of Metal Compound Clusters

While fixed-frequency photodissociation provides interesting qualitative information about cluster structure, it is desirable to measure spectra for these species that can be compared to the predictions of theory. Only then can suspected structures be confirmed with confidence. However, although we have had success with spectroscopy on metal-ligand complexes, it is quite difficult to obtain vibrational spectroscopy for metal atom clusters that have no ligands. The vibrations in pure metal clusters occur at very low frequencies (100-400 cm^{-1}),[130,131] while those for carbide, oxide, and silicides may be found at somewhat higher frequencies. Our previous work on metal carbide and oxide clusters[37-44] used the FELIX free electron laser to cover the required wavelength region of 400-1800 cm^{-1}. However, in the last several years we have found that the IR-REMPI technique employed for those experiments only works for a few carbide and oxides, while photodissociation experiments are needed to study other systems. In both IR-REMPI and photodissociation experiments, the FELIX laser linewidth and the high laser powers required for multiphoton processes leads to broad lines and red-shifted vibrational resonances.[41] For example, although we reported spectra for Ti_8C_{12} some time ago, the exact structure of this cluster (D_{2d} versus T_d) is still not known.[37,41] Multiplet structure predicted by theory in the 1400 cm^{-1} region cannot be resolved by the FELIX experiment. It is therefore desirable to have a better laser source for IR spectroscopy in the fingerprint region.

Our present IR OPO systems have good linewidth (0.3 cm^{-1}) and are easy to use, but the wavelength coverage at present is limited to about 2000-4500 cm^{-1}. This works well for the vibrations that occur at higher frequencies for many small molecules, and this is why we have focused our work to date on metal-ligand complexes. However, we have recently obtained a new OPO crystal ($AgGaSe_2$) that provides expanded IR wavelength coverage (600-1900 cm^{-1}) via difference frequency generation between the present OPO oscillator signal beam and the 1.06 μ pump laser. Although the conversion efficiency is not as good as that at higher frequencies, we can produce 20-400 μJ/pulse in this region. In our collaborative project with Mark Johnson, we have recently studied protonated water clusters, $H^+(H_2O)_n$ in the 600-2000 cm^{-1} region,[132] and the IR pulse energy from this $AgGaSe_2$ OPO was enough to obtain good signals for these mass-selected ions (via multipass excitation and argon tagging methods). Our crystal is already installed and working, and when some data acquisition programming issues are fixed, we will be ready to measure spectra. Extension of experiments all the way down to 600 cm^{-1} will require new windows (AR-coated ZnSe) to replace our current CaF windows (these don't transmit below 1000 cm^{-1}).

We plan to use this new IR laser source to measure spectra for mass-selected cations of the carbide and oxide clusters, in much the same way that we have already studied metal-ligand complex ions. We will prepare clusters of the form $M_nX_m^+$ (X=C,O) tagged with argon or neon, e.g., $M_nX_m^+$-RG_x. M-C, M-O, C-C and O-O stretch vibrations are known to occur in the 600-1900 cm^{-1} region covered by this laser, and excitation of these can lead to the loss of one or more rare gas atoms. We will first examine some of the same systems studied already at lower resolution with the free electron laser, e.g., $M_8C_{12}^+$, (M=Ti,V,Zr) which have strong resonances[40] near 1400 cm^{-1}; $(Al_2O_3)_n$ which have bands[44] near 900 cm^{-1}; $Nb_nO_m^+$ which have bands[46] at 800 and 1000 cm^{-1}; etc. Carbides and oxides will generally have higher vibrational frequencies than silicides, and so we will focus on these species first. At the lower energies of the IR excitation here, the binding of argon may be strong enough so that its elimination is not efficient. However, in such cases we find that multiple argon attachment or neon tagging can overcome this limitation. The IR-REMPI method could only study clusters above 20 or so atoms, but IR photodissociation works for smaller species that are easier to handle with theory. It should be possible to measure spectra for clusters with only a few atoms (e.g., VC_2^+, $V_2C_4^+$) up to those with 20 or more atoms for the same metal compound system. Likewise, many of the newer results for cations have been done in the mode of parent ion depletion because full mass-selection was not available. However, we detect the fragments from selected parent ions on a zero background, and therefore have higher sensitivity. In experiments so far, we have large enough signals so that ions are integrated with an oscilloscope, but counting electronics are available if needed.

Infrared Spectroscopy of Metal-Ligand Adducts

As noted above, metal oxides are important in surface science and catalysis,[64-68] both because of their own intrinsic reactivity and because these materials are important as supports for metal nanoparticle catalysts. Nanocatalysis has become an important subfield of cluster research, motivated in particular by the surprising behavior of small gold clusters deposited on metal oxides, as reported first by Haruta and coworkers.[133] While there has been a tremendous effort aimed at the surface science of supported gold clusters,[134-144] and gas phase reactions of small metal oxides and gold clusters have been studied,[145-149] there is virtually no spectroscopy of this adsorption chemistry on gas phase clusters. Our metal-molecular infrared measurements are ideally suited to probe the details of molecular adsorption in these systems. Likewise, our synthesis program also requires knowledge of ligand interactions on compound nanoparticles. Therefore, we will employ IR spectroscopy to probe molecular adsorbates on metal oxide systems and on noble metal clusters.

The mechanism of the reactivity of oxide-supported gold clusters is believed to involve charge injection from the oxide surface into the gold clusters, making these clusters more negative.[135,144] This takes place most effectively when the cluster is supported on a defect site on the oxide surface. To probe the fundamental interactions involved, we will systematically study the IR spectroscopy of adsorbate molecules on small oxide clusters, on pure gold clusters and on gold-oxide mixtures. Silver and copper studies will also be done to complement the gold work. We will focus on some of the same oxide metals (Ti, Mg, V) and adsorbate molecules (CO, CO_2, ethylene, acetylene, etc.) studied in the previous surface chemistry on these systems. Based on our prior experience with various metal-ligand clusters and with the production of compound and mixed-metal clusters, we anticipate no problem in producing the desired species. The issues of charging suggest that we should investigate both the corresponding cation and anion clusters. Although we work mostly on cations, extension of our experiments to anions is also feasible.

The asymmetric stretch of CO_2 has already been studied in our lab on many metal ions[90,94,96,97,99,104] and also on nickel-oxide ions,[97] and this mode is accessible with our present OPO system. Likewise C-H stretch vibrations have already been studied by our group in many metal complexes.[93,103,105,107,111] In acetylene and ethylene complexes, isomeric species (vinylidene, ethylidyne) may be formed,[64] and the IR would identify these structures. C-O and C-C stretches are likely to occur at frequencies below 2000 cm^{-1}, and these will be accessible with the new $AgGaSe_2$ OPO configuration. We suspect that adsorbed O_2 may also be detected in the low frequency range; our recent studies of N_2 adsorbed on vanadium show that the N-N stretch achieves high IR activity when attached to metal.[108] Most of our experiments to date have focused on small metal systems, but we have recently reported a study of the bending mode of water adsorbed on vanadium clusters in the size range up to 18 metal atoms.[150] Although infrared spectroscopy on metal systems is becoming more popular, and there are several studies of adsorbates on metal clusters that have been done with free electron lasers,[46,151-152] our research group is presently the only one with metal cluster sources and the new OPO technology needed to attack these problems with higher spectral resolution. Related to this work, Castleman and coworkers[153] have studied the reaction kinetics of small hydrocarbons interacting with V, Ta and Nb oxide cation clusters. It will therefore be interesting to probe the spectroscopy of the reactive versus non-reactive clusters to complement this work.

Synthesis of Ligand-Coated Clusters

The general strategy of our synthetic program was described earlier, and the apparatus is shown in Figure 7. Our primary targets for isolation are the metal carbide, oxide and silicide clusters of the transition metals, which we will produce in the flow reactor and stabilize with ligand coatings. A major focus will be on the M_8C_{12} met-car and the $M_{14}C_{13}$ nanocrystal species, which are most stable for the metals Ti, V, Zr.

Although there have been many attempts to isolate these species via arc discharge methods, they continue to elude isolation. We have had evidence in some experiments that we made small amounts of Ti_8C_{12} coated with ethylenediamine, but these results were not reproducible. With the new mass spectrometry diagnostics, we hope to have better control to optimize conditions and more success. Our results on metal oxides have been more productive, and we have been able to make ligand-coated titanium and vanadium oxide clusters reproducibly. The titanium system produced complexes containing from only two or three metal atoms up to nm and even micron diameter particles (imaged with TEM). These results suggest that many other transition metal oxides will be accessible via our methodology. We have not yet attempted metal-silicon cluster isolation, but these systems are also interesting.

The choice of ligand material for nanoparticle coatings is a crucial aspect of these studies. To date, we have tried THF and ethylenediamine for these experiments. THF reacted with titanium and vanadium, producing oxides when no other source of oxygen was present.[127] Ethylenediamine was much less reactive, and attached to metal without fragmentation.[127] We will therefore focus on other mono- and bidentate ligands with nitrogen coordination as our next approach for these systems. We will seek guidance from able inorganic chemists in our department and elsewhere to make up for our limited abilities as synthetic chemists.

The initial characterization of ligand-coated nanoparticle solutions will take place with our remote laser desorption mass spectrometer, as noted before. As systems are optimized with the on-line mass spectrometer diagnostics and produced in greater quantities, we can extend the analysis to conventional spectroscopy (IR, UV-VIS, NMR) and imaging systems (SEM, TEM, AFM), all of which are available in our department.

We also have access to laser desorption with high resolution FT-MS analysis via instruments located in the lab of Dr. Jon Amster (also at UGA). Exact mass measurements and isotope patterns make it possible to determine the number of metal atoms present when there are nominal metal-ligand mass coincidences.

The outlook for these synthesis experiments is much less certain than our molecular beam experiments. However, the LAFR methodology represents a distinctly different approach to nanoparticle synthesis, and the results so far are very promising. With the new mass spectrometer system, we should be able to optimize conditions and produce clusters more efficiently and reproducibly than before. Although this work is risky, its potential payoffs are significant.

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Principle Investigator Time

The PI, Professor Michael A. Duncan, is budgeted for 2/3 research and 1/3 teaching during the regular academic year. This means that his regular teaching load is one class with three contact hours per week. He is budgeted for 100% research in the summer, with no teaching other than the supervision of graduate students.

Duncan's research time is divided between three project areas supported with major grants (AFOSR, NSF, DOE). There is some slight overlap between the present project and the DOE project, as both have a component of IR spectroscopy on cluster adsorbate complexes. Approximately 1/3 of Duncan's research time will be spent on the proposed work during both the academic year and the summer.

The Duncan research group consists of eight graduate students, two undergraduate research students and no postdoctoral fellows. Two of the grad students are supported by the present AFOSR project. Two Ph.D. students presently in their second and third year (Prosser Carnegie –B.S. Wofford College and Tim Ayers – B.S. University of West Georgia) will be supported if this project is renewed. One student will focus on the gas phase work and one will focus on the synthetic work.

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Professional Appointments

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1983 Assistant Professor, University of Georgia
1988 Associate Professor, University of Georgia
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